

JCO5 Rec'd PCT/PTO 05 SEP 2001

FORM PTO-1390
(REV 11-2000)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

**TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371**

ACR2691P1US

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

09/914942

INTERNATIONAL APPLICATION NO.

PCT/EP00/01738

INTERNATIONAL FILING DATE

28 February 2000

PRIORITY DATE CLAIMED

5 March 1999

TITLE OF INVENTION

ESTERQUATS, THEIR INTERMEDIATES, A PROCESS TO MAKE THE ESTERQUATS, AND THEIR USE

APPLICANT(S) FOR DO/EO/US

Hartmut Ahrens and Manfred Josef Bergfeld

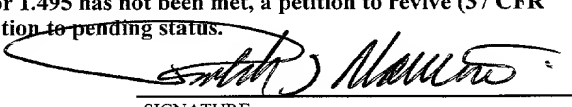
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☐ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☒ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☐ is attached hereto.
 - b. ☒ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☐ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). **(unsigned)**
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11 to 20 below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
14. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information:
 1. **Version with Markings to Show Changes Made**
 2. **Copy of International Preliminary Examination Report dated 9 July 2001**

Express Mail Label No.: EM122094767US

U.S. APPLICATION NO. (if known, see 37 CFR 1.5) 09/914942		INTERNATIONAL APPLICATION NO. PCT/EP00/01738		ATTORNEY'S DOCKET NUMBER ACR2691P1US	
21. <input checked="" type="checkbox"/> The following fees are submitted: BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)): Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$1000.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$860.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$710.00 International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$690.00 International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00 ENTER APPROPRIATE BASIC FEE AMOUNT =				CALCULATIONS PTO USE ONLY	
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	\$	
Total claims	13 - 20 =	---	x \$18.00	\$ ---	
Independent claims	1 - 3 =	---	x \$80.00	\$ ---	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)				+ \$270.00	
TOTAL OF ABOVE CALCULATIONS =				\$ 860.00	
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.				\$	
SUBTOTAL =				\$ 860.00	
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$	
TOTAL NATIONAL FEE =				\$ 860.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +				\$	
TOTAL FEES ENCLOSED =				\$ 860.00	
				Amount to be refunded:	\$
				charged:	\$
a. <input type="checkbox"/> A check in the amount of \$ _____ to cover the above fees is enclosed. b. <input checked="" type="checkbox"/> Please charge my Deposit Account No. <u>01-1350</u> in the amount of \$ <u>860.00</u> to cover the above fees. A duplicate copy of this sheet is enclosed. c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>01-1350</u> . A duplicate copy of this sheet is enclosed. d. <input type="checkbox"/> Fees are to be charged to a credit card. WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.					
NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.					
SEND ALL CORRESPONDENCE TO: Ralph J. Mancini Akzo Nobel Inc. Intellectual Property Department 7 Livingstone Avenue Dobbs Ferry, NY 10522-3408 (914) 674-5465					
				 SIGNATURE	
				Ralph J. Mancini NAME	
				34,054 REGISTRATION NUMBER	

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PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application of:

Ahrens, H. et al.

: Docket No.: ACR 2691P1 US

Serial No.: Unassigned

Int'l Application No.: PCT/EP00/01738

: Group Art Unit:

Int'l Filing Date: 28 February, 2000

Priority Date: 5 march, 1999

: Examiner:

Title: ESTERQUATS, THEIR INTERMEDIATES,
A PROCESS TO MAKE ESTERQUATS, AND
THEIR USE

Assistant Commissioner of Patents

Washington, D.C. 20231

PRELIMINARY AMENDMENT

Sir:

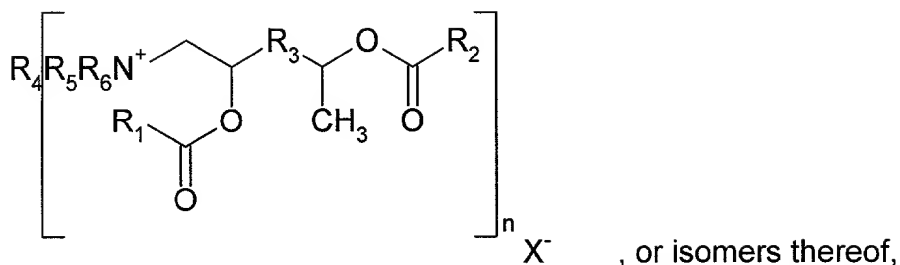
In accordance with the provisions of 37 C.F.R. §1.111, applicants provide the following amendments and remarks for entry in the above-identified case.

IN THE CLAIMS

Please cancel claim 11.

Please amend the claims as follows:

2. Compounds according to claim 1 of the formula



wherein R_1 and R_2 are independently selected from linear or branched, saturated or unsaturated C_{6-22} hydrocarbyl,

R_3 is nothing or C_{1-20} hydrocarbyl,

R_4 is C_{1-6} alkyl, C_{1-6} alkylene, or independent Z,

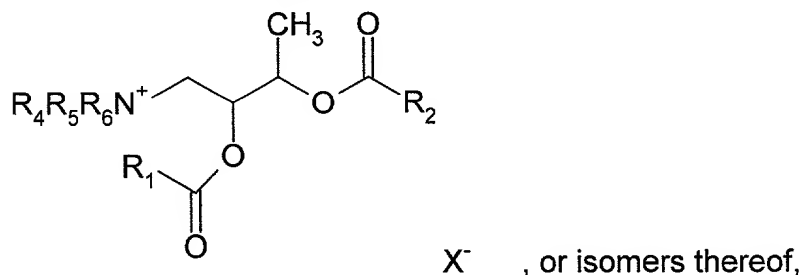
R_5 is H, C_{1-6} alkyl, independent Z, or the residue of the quaternizing agent, such as C_{1-30} alkyl or alkenyl, preferably, C_{1-7} alkyl or alkenyl,

R_6 is C_{1-6} alkyl or independent Z,

n is 1 or 2, and

X^- is an ion selected from Cl^- , Br^- , I^- , F^- , $CH_3SO_4^-$, $C_2H_5SO_4^-$, $H_2PO_4^-$, HPO_4^{2-} , PO_4^{3-} , $H_2PO_3^-$, HPO_3^{2-} , $H_2PO_2^-$, HPO_2^{2-} , nitrate⁻, formate⁻, acetate⁻, propionate⁻, tartrate⁻ and benzoate⁻, wherein the total charge of the anions equals the total charge of the cations.

3. Compounds according to claim 2 of the formula



wherein R_1 , R_2 , R_4 - R_6 and X^- have the meaning given in claim 1 wherein R_1 and R_2 are independently selected from linear or branched, saturated or unsaturated C_{6-22} hydrocarbyl,

R_4 is C_{1-6} alkyl, C_{1-6} alkylene, or independent Z,

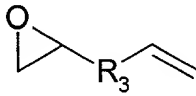
R₅ is H, C₁₋₆ alkyl, independent Z, or the residue of the quaternizing agent, such as C₁₋₃₀ alkyl or alkenyl, preferably, C₁₋₇ alkyl or alkenyl,

R₆ is C₁₋₆ alkyl or independent Z,

and

X⁻ is an ion selected from Cl⁻, Br⁻, I⁻, F⁻, CH₃SO₄⁻, C₂H₅SO₄⁻, H₂PO₄⁻, HPO₄²⁻, PO₄³⁻, H₂PO₃⁻, HPO₃²⁻, H₂PO₂⁻, HPO₂²⁻, nitrate⁻, formate⁻, acetate⁻, propionate⁻, tartrate⁻ and benzoate⁻, wherein the total charge of the anions equals the total charge of the cations..

4. Compounds according to claim 1 wherein R₁ and R₂ are independently selected from linear or branched, saturated or unsaturated C₁₂₋₁₈ alkyl groups.
5. Compounds according to claim 1, wherein R₄ and R₆ are methyl.
6. Compounds according to claim 1 wherein X⁻ is chloride, methyl sulfate or ethyl sulfate.
7. Intermediates for making one or more of the compounds of claim 1 wherein said intermediate has the formula R₄[R₆NZ]_n, wherein R₄, R₆, n, and Z have the meaning given in claim 1.
8. A fabric softening composition comprising one or more of the compounds according to claim 1.
9. A process of making the compounds of claim 1 which comprises:

- reacting an unsaturated epoxide of the formula  with an amine or protonated amine of the formula R₄[R₅R₆N]_n or R₄[R₅R₆N⁺H]_n X⁻, wherein R₃, R₄, R₅, R₆, n, and X⁻ have the meaning given in claim 1, and

- esterification of the intermediate with, on average, 1-2 moles of fatty acid derivatives, comprising the moieties $R_1-C(O)-$, $R_2-C(O)-$ or mixtures thereof, per mole of OH groups of the intermediate,
 - an optional conventional quaternization either before or after said esterification step.
10. The process according to claim 9, wherein a trialkylamine is reacted with the unsaturated epoxide.
12. A fabric softening composition which comprises at least one compound according to claim 2 .
13. The composition of claim 12 which additionally comprises at least one performance booster selected from the group consisting of cationic and non-ionic surfactants.

Please add the following new claim 14:

14. The composition of claim 8 which additionally comprises at least one performance booster selected from the group consisting of cationic and non-ionic surfactants.

Remarks

This is an international application filed under the Patent Cooperation Treaty (PCT) on February 28, 2000. The claims have been amended herein in order to eliminate multiple dependencies and to place them in ideal condition for U.S. prosecution.

Attached hereto is a marked-up version of the changes made to the specification and claims by the current amendment. The attached page is captioned **"Version with markings to show changes made."**

Since the present amendment raises no new issues and presents no new matter, entry thereof in accordance with 37 C.F.R. §1.111 prior to the initial examination of the present case on the merits is respectfully requested.

Respectfully submitted,



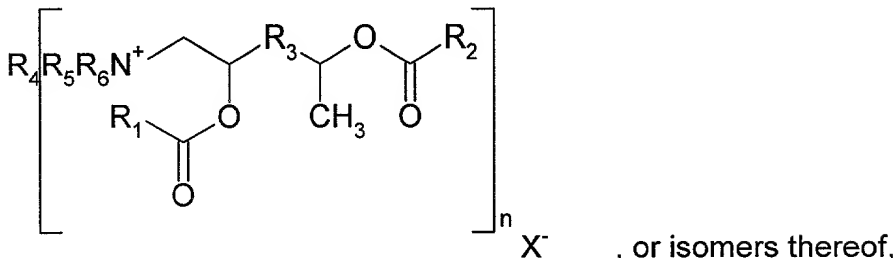
Ralph J. Mancini
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"Version with markings to show changes made."

2. Compounds according to claim 1 of the formula



wherein R_1 and R_2 are independently selected from linear or branched, saturated or unsaturated C_{6-22} hydrocarbyl,

R_3 is nothing or C_{1-20} hydrocarbyl,

R_4 is C_{1-6} alkyl, C_{1-6} alkylene, or independent Z,

R_5 is H, C_{1-6} alkyl, independent Z, or the residue of the quaternizing agent, such as C_{1-30} alkyl or alkenyl, preferably, C_{1-7} alkyl or alkenyl,

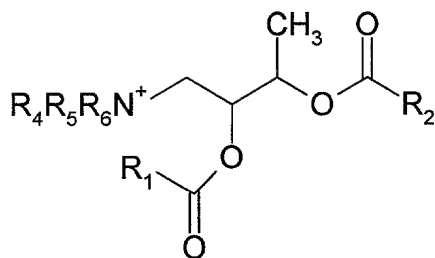
R_6 is C_{1-6} alkyl or independent Z,

n is 1 or 2, and

X^- is an ion selected from Cl^- , Br^- , I^- , F^- , $CH_3SO_4^-$, $C_2H_5SO_4^-$, $H_2PO_4^-$, HPO_4^{2-} , PO_4^{3-} , $H_2PO_3^-$, HPO_3^{2-} , $H_2PO_2^-$, HPO_2^{2-} , nitrate⁻, formate⁻, acetate⁻, propionate⁻, tartrate⁻ and benzoate⁻, wherein the total charge of the anions equals the total charge of the cations.

R_1 , R_6 , n , and X^- have the meaning given in claim 1.

3. Compounds according to claim 2 of the formula



X^- , or isomers thereof,

wherein R_1 , R_2 , $\text{R}_4\text{-R}_6$ and X^- have the meaning given in claim 1 wherein R_1 and R_2 are independently selected from linear or branched, saturated or unsaturated C_{6-22} hydrocarbyl,

R_4 is C_{1-6} alkyl, C_{1-6} alkylene, or independent Z,

R_5 is H, C_{1-6} alkyl, independent Z, or the residue of the quaternizing agent, such as C_{1-30} alkyl or alkenyl, preferably, C_{1-7} alkyl or alkenyl,

R_6 is C_{1-6} alkyl or independent Z,

and

X^- is an ion selected from Cl^- , Br^- , I^- , F^- , CH_3SO_4^- , $\text{C}_2\text{H}_5\text{SO}_4^-$, H_2PO_4^- , HPO_4^{2-} , PO_4^{3-} , H_2PO_3^- , HPO_3^{2-} , H_2PO_2^- , HPO_2^{2-} , nitrate $^-$, formate $^-$, acetate $^-$, propionate $^-$, tartrate $^-$ and benzoate $^-$, wherein the total charge of the anions equals the total charge of the cations..

4. Compounds according to ~~any one of claims 1-3~~ wherein R_1 and R_2 are independently selected from linear or branched, saturated or unsaturated C_{12-18} alkyl groups.

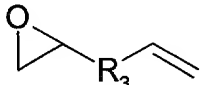
5. Compounds according to ~~any one of the preceding claims 1~~, characterized in that wherein R_4 and R_6 are methyl.

6. Compounds according to ~~any one of the preceding claims 1~~ wherein X^- is chloride, methyl sulfate or ethyl sulfate.

7. Intermediates for making one or more of the compounds of the preceding claims 1 wherein said intermediate has according to the formula $R_4[R_6NZ]_n$, wherein R_4 , R_6 , n , and Z have the meaning given in claim 1.

8. A fabric softening composition ~~Compositions comprising one or more of the compounds according to any one of the preceding claims 1.~~

9. A process of making ~~to make~~ the compounds of claim 1 which comprises~~comprising the steps of:~~

- reacting an unsaturated epoxide of the formula  with an amine or protonated amine of the formula $R_4[R_5R_6N]_n$ or $R_4[R_5R_6N^+H]_n X^-$, wherein R_3 , R_4 , R_5 , R_6 , n , and X^- have the meaning given in claim 1, and
- esterification of the intermediate with, on average, 1-2 moles of fatty acid derivatives, comprising the moieties $R_1-C(O)-$, $R_2-C(O)-$ or mixtures thereof, per mole of OH groups of the intermediate,
- an optional conventional quaternization either before or after said esterification step.

10. ~~The~~A process according to claim 9, characterized in that wherein a trialkylamine is reacted with the unsaturated epoxide.

12. A fabric softening composition which comprises at least one ~~Use of a compound or composition according to any one of claims 2 1-8 as a fabric softener.~~

13. The composition of ~~Use according to claim 12 wherein the compound is used in which additionally comprises combination with a conventional at least one~~ performance booster selected from the group consisting of cationic and non-ionic surfactants.

New Claim:

14. The composition of claim 8 which additionally comprises at least one performance booster selected from the group consisting of cationic and non-ionic surfactants.

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ESTERQUATS, THEIR INTERMEDIATES, A PROCESS TO MAKE THE
ESTERQUATS, AND THEIR USE

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The invention relates to specific quaternary ammonium compounds having at least one nitrogen-bonded moiety with at least one ester function (esterquats), to intermediates for making such esterquats, to compositions comprising one or more of these esterquats, to a process to make them, and to the use of the esterquats as a fabric softener.

10

Quaternary ammonium compounds having a substituent on the nitrogen atom with two ester groups are known. Also compositions comprising such ammonium compounds are known. WO 97/47588, for instance, discloses how 2,3-dihydroxypropyl trimethyl ammonium chloride is reacted with lauric acid to form a composition comprising the corresponding diester quaternary compound, a propyl-diester-quat (PDQ).

15

The use of PDQ as a fabric softener is known to result in a very good softening performance. However, the manufacture of these compounds is cumbersome and the raw material N,N-dimethyl-1-amino propane-2,3-diol is costly. Also, the epichlorohydrin typically used to make this raw material for PDQ is less desired from an environmental viewpoint. Furthermore, it is noted that the production of PDQ typically requires the use of a solvent, such as isopropanol, in the quaternization reaction. However, such solvent can transesterify with the PDQ, resulting in the formation of a contaminant (the fatty acid derivative of the solvent) and a reduction of the softening performance of the PDQ-containing product (because less diester compound is present). Therefore, there is a need for alternative compounds with a better price/performance that can be produced according to a process that puts less strain on the environment. Preferably, this

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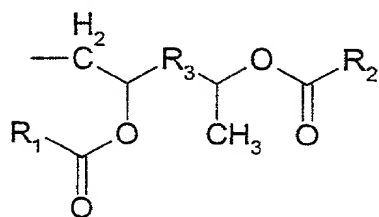
process does not require the use of solvents that can transesterify with fatty acid esters.

Our investigations have led us to a new and surprisingly simple process for making new types of quaternary compounds where at least one of the nitrogen substituents contains at least one ester group, and to new intermediates. These compounds, and compositions comprising these compounds, offer a good fabric softening performance and a better price/performance than the conventional fabric softeners. It is noted that the intermediates may be used as fabric softeners themselves. Also, the new process offers advantages from an environmental viewpoint because epichlorohydrin is not used. Furthermore, in one of the preferred embodiments the quaternization step of the amine is not performed towards the end of the synthesis of the surface-active compound, but already on the low-molecular weight amine. The process is improved by this, because it is much simpler to separate and purify the low-molecular weight quaternized amine than to perform such steps on the resulting surface-active compound, if so desired. More specifically, during the processing/washing of a surface-active compound, there is a tendency on the part of the compound to disperse. In another preferred embodiment, a trialkylamine is reacted with an epoxy alkene in the presence of an acid, in order to produce a quaternary intermediate. The process of this preferred embodiment obviates the use of epichlorohydrin as well as the use of undesired solvents. The quaternary intermediate can be esterified to give the preferred diesterquat fabric softeners. However, the monoesterquat that is formed may be useful as a fabric softener as well.

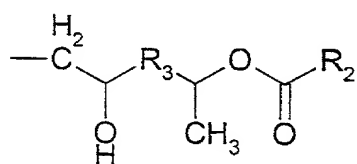
The new quaternary compounds according to the invention are of the formula:



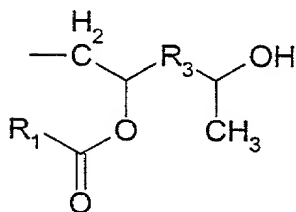
wherein Z is covalently bonded to the nitrogen atom, and of the following formulae (I-IV)



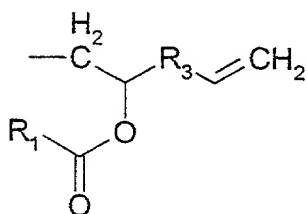
(I),



(II)

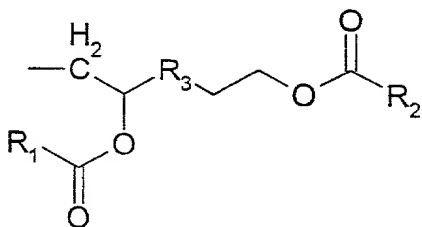


(III)

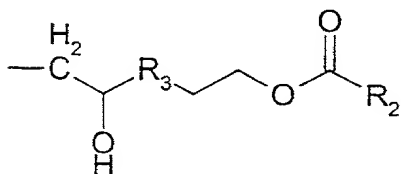


(IV)

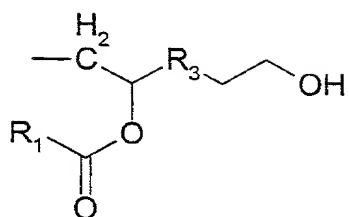
or isomers thereof with the formulae:



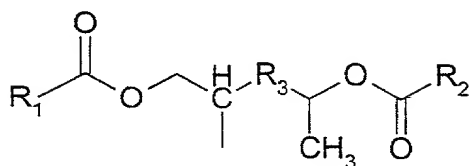
(Ia)



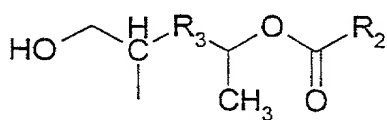
(IIa)



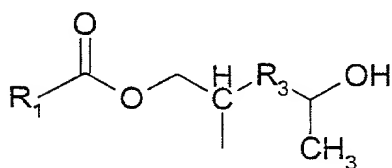
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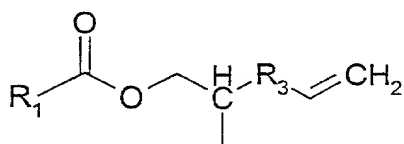
(Ib),



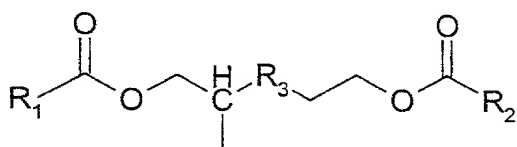
(IIb)



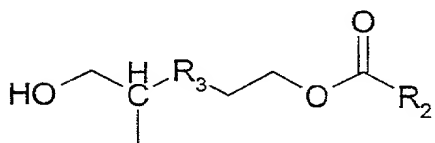
(IIIb)



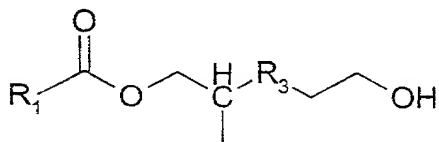
(IVb)



(Ic)



(IIc), and



(IIIc)

wherein,

replacement sheet

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5

R_1 and R_2 are independently selected from linear or branched, saturated or unsaturated C_{6-22} hydrocarbyl,

R_3 is nothing or C_{1-20} hydrocarbyl,

R_4 is C_{1-6} alkyl, C_{1-6} alkylene, or independent Z,

5 R_5 is H, C_{1-6} alkyl, independent Z, or the residue of the quaternizing agent, such as C_{1-30} alkyl or alkenyl, preferably, C_{1-7} alkyl or alkenyl,

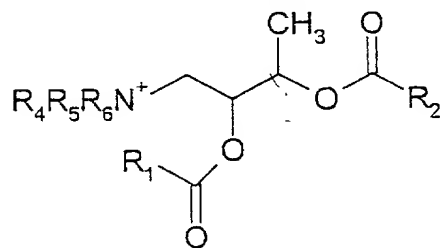
R_6 is C_{1-6} alkyl or independent Z,

n is 1 or 2, and

10 X^- is an ion selected from Cl^- , Br^- , I^- , F^- , $CH_3SO_4^-$, $C_2H_5SO_4^-$, $H_2PO_4^-$, HPO_4^{2-} , PO_4^{3-} , $H_2PO_3^-$, HPO_3^{2-} , $H_2PO_2^-$, HPO_2^{2-} , nitrate⁻, formate⁻, acetate⁻, propionate⁻, tartrate⁻ and benzoate⁻, wherein the total charge of the anions equals the total charge of the cations. The compounds may be used after purification and/or isolation. Preferably, they are part of a composition comprising more than one of the compounds of formulae I-IV and isomers thereof, since extensive

15 isolation steps for the individual compounds can then be refrained from. Purification may include a bleaching and/or adsorption step to convert and/or remove chemicals that cause discolouration.

Preferred are compounds of formula (I), given in full below



20

 X^- (V)

or isomers thereof, wherein R_1-R_6 have the meaning as presented above.

More preferably, the compounds of the above formulae I-IV, or the isomers thereof, are of the formula wherein R_1 and R_2 are C_{12-18} . Even more preferably,

25 R_1 and R_2 have a carbon distribution within the range such as can be found in

commercial fatty acids. Also preferred compounds of formulae I-IV or isomers thereof are those of the formula wherein R_4 and R_6 are methyl or ethyl.

Other preferred compounds of formulae I-IV or isomers thereof are those of the formula wherein R_5 is methyl or ethyl.

5 Preferably, n is 1.

Further preferred compounds of formulae I-IV or isomers thereof are those of the formula wherein X^- is chloride, methyl sulfate, or ethyl sulfate.

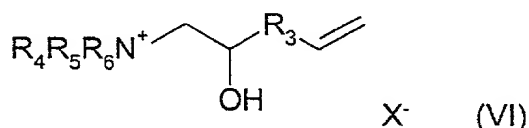
10 Another embodiment of the invention is the process to make the compounds according to formulae I-IV and/or isomers thereof. This process involves the reaction of an unsaturated epoxide with an amine, preferably a dialkylamine or trialkylamine, after which the unsaturated, hydroxy group-substituted intermediate is reacted with, on average, 1-2 moles of fatty acid groups per mole of hydroxy group of the intermediate to form an ester. Using this ratio of
15 fatty acid groups will ensure that at least some of the unsaturated bonds are reacted as well to form the preferred diesters.

It is noted that F.F. Blicke and J.H. Biel in *J. Am.Chem.Soc.* 79, 5508-5512 (1957) disclose that 1,2-epoxy-3-butene can be reacted with aqueous
20 dimethylamine hydrochloride to form 1-dimethylamino-2-hydroxy-3-butene. However, it is not disclosed that such a compound can be further reacted with 1-2 moles of fatty acid per mole of this product to form the compounds according to the invention with good fabric softening performance.

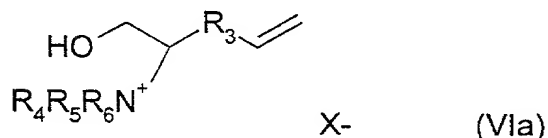
25 Another embodiment of the invention concerns amines that can be formed as intermediates by reacting a dialkylamine with an unsaturated epoxide, followed by esterification. These intermediates are of the formula $R_4[R_6NZ]_n$, wherein R_4 , R_6 , n , and Z have the meaning specified above. These intermediates may be used as fabric softeners themselves. However, preferably they are quaternized

in conventional ways with agents of the formula R_5X , in order to give the preferred products of the formulae I-IV and isomers thereof.

Intermediate products formed by reacting a trialkylamine with an unsaturated epoxide in the presence of an acid are preferably of the formula



or the isomers thereof according to the formula



wherein R_3 - R_6 and X have the meaning specified above.

These intermediates can be easily transformed into the desired compounds of formulae I-IV by direct or trans-esterification. The products of formula VI, or the isomers thereof, may themselves be used as a fabric softener. Therefore, a composition comprising compounds I-IV may also contain intermediates of formula VI, without the fabric softening properties being adversely affected.

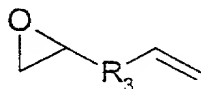
15

A further embodiment of the present invention constitutes the use of the compounds according to formulae I-VI, or the isomers thereof, as a fabric softener. Preferably, the compounds are compounds of formula I or the isomers thereof. The products are well-suited for this use because of their expected biodegradability, due to the two ester functions in the molecule, and their price/performance. It is noted that it is known in the art to further improve the performance of fabric softening compositions by combining the fabric softening compounds with a performance booster selected from the group consisting of cationic and non-ionic surfactants. When used in this fashion, the fabric softening compounds are even more effectively deposited on the textile fabric.

The amine that is reacted with the unsaturated epoxide is of the structure $R_4[R_5R_6N]_n$, or the protonated form thereof with structure $R_4[R_5R_6N^+H]_n X^-$, wherein R_4 , R_5 , R_6 , n , and X^- have the meaning defined above. Preferably, a dialkylamine or trialkylamine is reacted with the unsaturated epoxide.

- 5 Preferably, n is 1. Of the amines with n is 2, ethylene diamine is preferred.

The unsaturated epoxides that can be used are preferably 1,2-epoxyalkenes of the formula



wherein R_3 has the meaning defined above.

- 10 Preferred 1,2-epoxyalkenes are 1,2-epoxy-3-butene, 1,2-epoxy-4-pentene, 1,2-epoxy-5-hexene, 1,2-epoxy-6-heptene, 1,2-epoxy-3-pentene, 1,2-epoxy-3-hexene, 1,2-epoxy-3-heptene, and 1,2-epoxy-4-hexene. More preferred 1,2-epoxyalkenes are 1,2-epoxy-3-butene, 1,2-epoxy-3-pentene, 1,2-epoxy-3-hexene, and 1,2-epoxy-3-heptene. Most preferred is 1,2-epoxy-3-butene.

15

- At least n mole of 1,2-epoxyalkene is to react with one mole of $R_4[R_5R_6N]_n$, or the protonated form thereof with structure $R_4[R_5R_6N^+H]_n X^-$, according to the invention. However, if a monoalkylamine or ammonia is used to make the indicated dialkylamine or trialkylamine *in situ* by first reacting it with 1,2-epoxyalkene, then up to four moles of 1,2-epoxyalkene can be reacted per mole of amine.
- 20

- The ester functions in the compounds of the invention typically are derived from saturated or unsaturated, linear or branched C_{6-30} , preferably C_{8-22} , more preferably C_{12-18} , most preferably naturally occurring, fatty acids, optionally substituted with, e.g., one or more hydroxy groups. Preferred fatty acids used in making the compounds of the invention include coconut, palm, palm kernel, soybean, oleic, tallow, rapeseed, canola, behenic, eruca fatty acids, and
- 25

mixtures thereof. Preferably, a fatty acid mixture comprising at least 50 percent by weight (%w/w) of C₁₂₋₁₈ fatty acids is used.

The acids may be used as such in a conventional direct esterification process, but also derivatives can be used, such as the corresponding acid chlorides or (mixed) anhydrides. In transesterification reactions typically a fatty acid ester is used. In such transesterification reactions preferably the methyl, ethyl and/or glycerol esters of the acids are used. Most preferred are mono-, di- and/or triglycerides of the acids. In the esterification process preferably a conventional (trans)esterification catalyst is used, such as hypophosphorous acid.

Preferably 50-100 percent, on a molar basis, of the hydroxy functions of the 1-amino-2-hydroxy-alkene intermediate formed after reacting amine and 1,2-epoxyalkene is esterified. More preferably, 75-100 mole percent of the hydroxy groups is esterified. Also, preferably 50-100 percent, on a molar basis, of the unsaturated functions of the 1-amino-2-hydroxy-alkene intermediate is reacted with fatty acid to give an ester function. More preferably, 75-100 mole percent of the alkene functions is esterified.

If a dialkylamine is used in the reaction with the 1,2-epoxyalkene, then the resulting diester bearing amine is to be quaternized in order to achieve the preferred fabric softening compounds according to the invention. The quaternization step is conventional, using agents of the formula R₅X, wherein R₅ and X have the meaning defined above. Examples of conventional quaternizing agents include, but are not limited to, dimethyl sulphate, diethyl sulphate, methyl chloride, methyl bromide, methyl iodide, benzyl chloride, benzyl bromide, allyl chloride, and allyl bromide.

However, in a preferred embodiment of the invention, the raw material is not a dialkylamine but a trialkylamine. When such trialkylamines are reacted with the unsaturated epoxide in the presence of a conventional activator for the ring

opening of epoxides, typically an acid, such as hydrochloric acid, sulfuric acid, hydrochloric salts of amines, the hydrochloric salt of pyridine, and the like, then the corresponding quaternary ammonium group-bearing unsaturated alcohol is formed. These alcohols can be converted to the corresponding mono- and/or diesterquaternary ammonium compounds by appropriate esterification. The esterification can be a direct esterification or a transesterification, both processes being known in the art for conventional esterification processes. Preferably, C₆₋₂₂ fatty acid groups are introduced into said esterification process, since such groups are needed to obtain the desired fabric softening effect.

The resulting quaternary ammonium compounds, having a nitrogen substituent with at least one ester group, can be used as is or after purification and/or isolation. The compounds, preferably the diester-bearing compounds, are pre-eminently suited for use as a biodegradable fabric softener.

The invention is elucidated by the following, non-optimized, examples.

Materials used:

Hypophosphorous acid ex Aldrich

Stearic acid ex Merck

Dimethylaminobutenol ex Eastman

Butadiene monoxide (1,2-epoxy-3-butene) ex Aldrich

Procedure

A mixture of N-(2-hydroxybut-3-en-1-yl)-N,N,N-trimethylammonium chloride and N-(1-hydroxybut-3-en-2-yl)-N,N,N-trimethylammonium chloride was produced by charging a 10 ml flask, equipped with a stirrer, with a mixture of 2.55 g (26.7 mmols) trimethylamine hydrochloride, 0.06 g (0.5 mmole) of 47.7 %w/w of trimethylamine in water, and 2 g water, and cooling the mixture to 10°C. Then

2.09 g (29.9 mmoles) of 1,2-epoxybutene were added dropwise during 1 hour while the temperature was maintained at 10°C. Thereafter, the mixture was heated to 40°C and further reacted for 2 hours. Subsequently, 1 ml of 1M HCl was added, after which the water was evaporated at atmospheric pressure. The
5 desired mixture remained.

Example 1

In a one-necked flask of 100 ml, equipped with stirrer and water separator, 1.58 g (10.2 mmoles) of a mixture of N,N-dimethyl-1-aminobut-3-en-2-ol
10 hydrochloride and N,N-dimethyl-2-aminobut-3-en-1-ol hydrochloride with a purity of 97.5 % by weight (%w/w) was combined with 6.07 g (21.4 mmoles) stearic acid. To the mixture, 1 ml of 50 %w/w of hypophosphorous acid in water was added as a catalyst. The mixture was stirred for 4 hours at 160°C at a reduced pressure of 1 mbar.

15 A mixture of 2,3-di(stearoyloxy)but-1-yl)dimethylamine hydrochloride and 1,3-di(stearoyloxy)but-2-yl)dimethylamine hydrochloride was formed with a yield of 24 mole%, based on the amino compound.

The product can be quaternized in conventional ways.

Example 2

In a one-necked flask of 100ml, equipped with stirrer and water separator, 1 ml of 50% by weight hypophosphorous acid in water was added to a mixture of 1.71 g (10.3 mmoles) N-(2-hydroxybut-3-en-1-yl)-N,N,N-trimethylammonium chloride/N-(1-hydroxybut-3-en-2-yl)-N,N,N-trimethylammonium chloride and
25 5.96 g (21.0 mmoles) stearic acid. With stirring, the mixture was reacted at 160°C for 4 hours under vacuum at a pressure of 1.33 mbar.

A mixture of 2,3-di(stearoyloxy)but-1-yl)trimethyl ammonium chloride (or 1-N,N,N-trimethylammoniumchloride-butane-2,3-distearate) and 1-3-di-

(stearoyloxy)but-2-yl)trimethylammonium chloride was formed with a yield of 49 mole%, based on the ammonium compound.

The product has good fabric softening properties.

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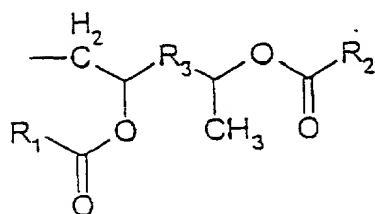
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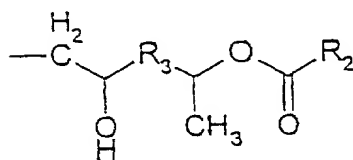
Claims

(52)

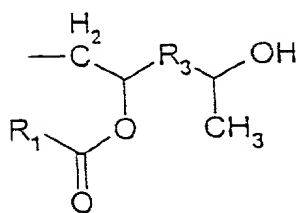
1. Quaternary ammonium compounds of the formula $R_4[R_5R_6N^+Z]_n X^-$,
 wherein Z is covalently bonded to the nitrogen atom and selected from the
 group of the following formulae (I-IV)



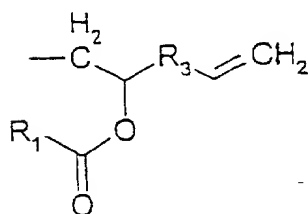
(I),



(II)



(III),



(IV),

10

and the isomers of any of these compounds, wherein

R_1 and R_2 are independently selected from linear or branched, saturated or unsaturated C_{6-22} hydrocarbyl,

R_3 is nothing or C_{1-20} hydrocarbyl,

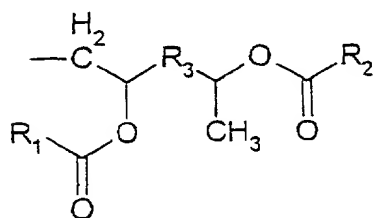
R_4 is C_{1-6} alkyl, C_{1-6} alkylene, or independent Z.

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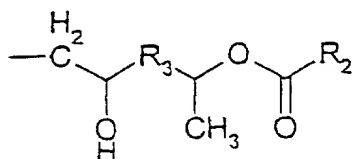
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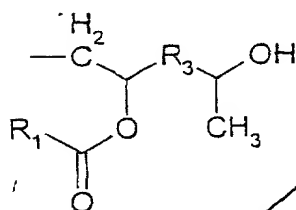
wherein Z is covalently bonded to the nitrogen atom, and of the following formulae (I-IV)



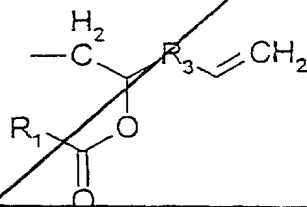
(I),



(II)

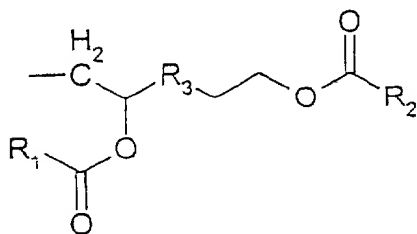


(III)

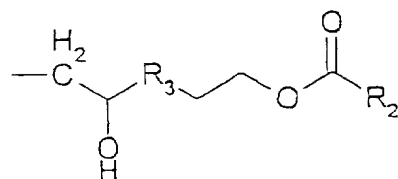


(IV)

isomers thereof with the formulae:



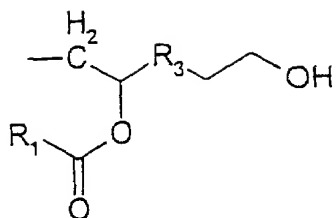
(Ia)



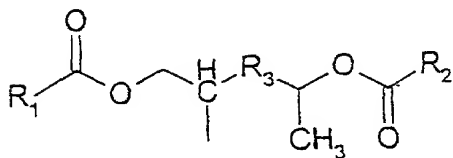
(IIa)

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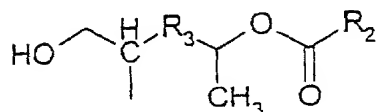
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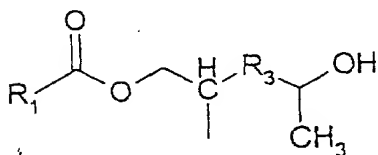
(IIIa)



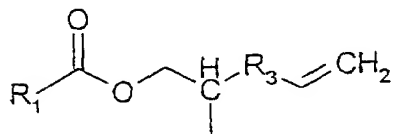
(Ib),



(IIb)

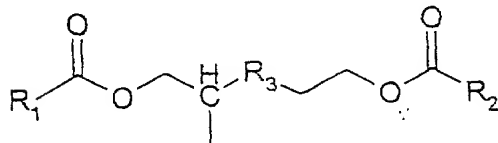


(IIIb)

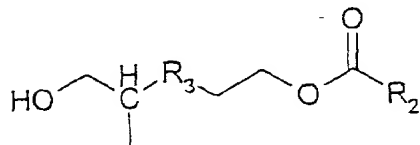


(IVb)

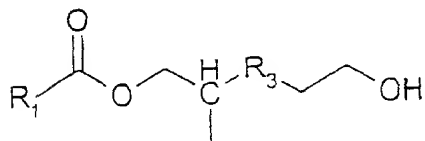
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(Ic)



(IIc), and



(IIIc)

wherein,

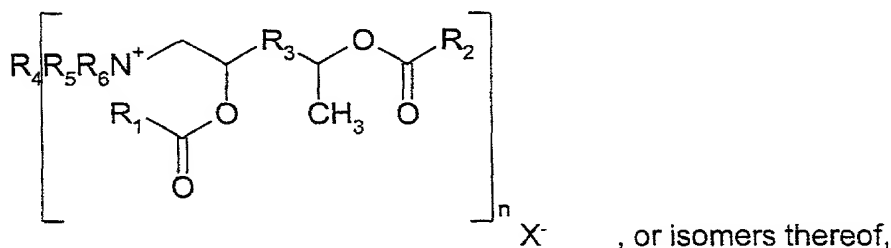
R_5 is H, C_{1-6} alkyl, independent Z, or the residue of the quaternizing agent, such as C_{1-30} alkyl or alkenyl, preferably, C_{1-7} alkyl or alkenyl,

R_6 is C_{1-6} alkyl or independent Z,

n is 1 or 2, and

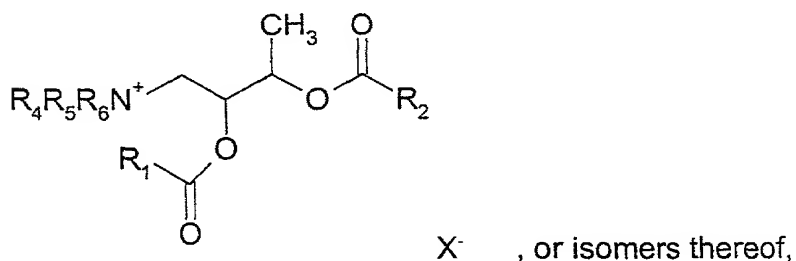
- 5 X^- is an ion selected from Cl^- , Br^- , I^- , F^- , $CH_3SO_4^-$, $C_2H_5SO_4^-$, $H_2PO_4^-$, HPO_4^{2-} , PO_4^{3-} , $H_2PO_3^-$, HPO_3^{2-} , $H_2PO_2^-$, HPO_2^{2-} , nitrate $^-$, formate $^-$, acetate $^-$, propionate $^-$, tartrate $^-$ and benzoate $^-$, wherein the total charge of the anions equals the total charge of the cations.

- 10 2. Compounds according to claim 1 of the formula



wherein R_1 - R_6 , n, and X^- have the meaning given in claim 1.

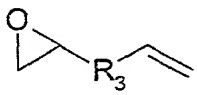
3. Compounds according to claim 2 of the formula



wherein R_1 , R_2 , R_4 - R_6 and X^- have the meaning given in claim 1.

4. Compounds according to any one of claims 1-3 wherein R_1 and R_2 are independently selected from linear or branched, saturated or unsaturated C_{12-18} alkyl groups.

5. Compounds according to any one of the preceding claims, characterized in that R_4 and R_6 are methyl.
6. Compounds according to any one of the preceding claims wherein X^- is chloride, methyl sulfate or ethyl sulfate.
7. Intermediates for making one or more of the compounds of the preceding claims according to the formula $R_4[R_6NZ]_n$, wherein R_4 , R_6 , n , and Z have the meaning given in claim 1.
8. Compositions comprising one or more of the compounds according to any one of the preceding claims.
9. A process to make the compounds of claim 1 comprising the steps of:



 - reacting an unsaturated epoxide of the formula $R_4[R_5R_6N]_n$ or $R_4[R_5R_6N^+H]_n X^-$, wherein R_3 , R_4 , R_5 , R_6 , n , and X^- have the meaning given in claim 1, and
 - esterification of the intermediate with, on average, 1-2 moles of fatty acid derivatives, comprising the moieties $R_1-C(O)-$, $R_2-C(O)-$ or mixtures thereof, per mole of OH groups of the intermediate,
 - an optional conventional quaternization either before or after said esterification step.
10. A process according to claim 9, characterized in that a trialkylamine is reacted with the unsaturated epoxide.
11. A process according to claim 9 or 10, characterized in that a product according to any one of claims 2-6 is formed.

12. Use of a compound or composition according to any one of claims 1-8 as a fabric softener.
- 5 13. Use according to claim 12 wherein the compound is used in combination with a conventional performance booster selected from the group consisting of cationic and non-ionic surfactants.

T03011 21571660

DECLARATION AND POWER OF ATTORNEY

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled: **ESTERQUATS, THEIR INTERMEDIATES, A PROCESS TO MAKE THE ESTER-QUATS, AND THEIR USE**

☒ was filed on **28 February 2000** as Appln Ser. No. **PCT/EP00/01738**

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above. All factual statements made in the specification of my own knowledge are true and all factual statements made on information and belief are believed to be true.

I acknowledge to the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, Sec. 1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, Sec. 119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Priority Claimed

<u>99200638.7</u>	<u>EUROPE</u>	<u>05 MARCH 1999</u>	<u> x </u> Yes <u> </u> No
(Number)	(Country)	(Day/Month/Year)	

I hereby claim the benefit under Title 35, United States Code § 119 of any provisional application(s) listed below:

_____ Appln. Ser. No.	_____ Country	_____ Day/Month/Year
--------------------------	------------------	-------------------------

I hereby claim the benefit under Title 35, United States Code, Sec. 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, Sec. 112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, Sec. 1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Appln. Ser. No.)	(Filing Date)	(Status: patented, pending, abandoned)
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POWER OF ATTORNEY: As a named inventor, I hereby appoint the following as my attorneys of record, with full power of substitution and revocation, to prosecute this application and to transact all business in the Patent Office:

Louis A. Morris, Reg. No. <u>28,100</u>	Richard P. Fennelly, Reg. No. <u>25,677</u>
Ralph J. Mancini, Reg. No. <u>34,054</u>	David H. Vickrey, Reg. No. <u>30,697</u>
Joan M. McGillicuddy, Reg. No. <u>35,608</u>	Lainie E. Parker, Reg. No. <u>36,123</u>

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(914) 674-5465

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further, that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Sec. 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

1-00
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Inventor's signature Hartmut Ahrens

Date 01.10.2001

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2-00

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Full name of third inventor _____

Inventor's signature _____

Date _____

Residence _____

Citizenship _____

Post Office Address _____

Full name of fourth inventor, if any _____

Inventor's signature _____

Date _____

Residence _____

Citizenship _____

Post Office Address _____